MASS-SPECTROMETRIC INVESTIGATION OF THE STRUCTURE OF A STOICHIOMETRIC $H_2/O_2/Ar$ FLAME DOPED WITH TRIMETYLPHOSPHATE AND N-TRIBUTYLPHOSPHATE

O.P. Korobeinichev, A.A. Chernov, V.M. Shvartsberg
Institute of Chemical Kinetics and Combustion
Siberian Branch Russia Academy of Sciences,
Novosibirsk,630090 Russia

ABSTRACT

Molecular beam mass-spectrometry was used to study the structure of a stabilized premixed H_2 / O_2 / Ar (25.4% / 12.7% / 61.9%) flame without and with additives (0.034% TMP-trimethylphosphate or TBP-tributylphosphate) at 80 torr (burner temperature: 85°C). The behavior of the TMP, TBP in flames and reactions leading to their destruction in flames have been studied. The promoting effect of the additive on the flame was observed, i.e. in the presence of the additive the combustion zone considerably decreases. Mass-spectrometric analysis of the species sampled from different flame zones, performed under soft ionization (at low ionization energies), was used to identify the intermediate and end products of the reactions destroying TMP in the flame, to measure the concentration profiles of some components in the flame related to these reactions. The data obtained testify that the primary products of the reaction of TMP destruction are either dimethylphosphate or dimethylphosphite or both of them. CH_3OH, CH_2O, CH_3O and the compound, the mass-spectrum of which contains the peak with m/e=80 (possibly, CH_5O_2P) were recorded as intermediates. The zone of TBP reacting in the flame is a bit narrower than that of TMP. Butene was registered as intermediate in an $H_2/O_2/Ar$ flame doped with TBP. The distributions of mass peak intensities with m/e=64 (HPO_2^+), 63 (PO_2^+), 48 (HPO^+), 47 (PO^+) in flames, characterizing the corresponding phosphorous containing components of the $H_xP_yO_z$ type were measured. The data obtained indicate the following sequence of the transformations of these components in flame:

$$HPO_2 , PO_2 \Rightarrow PO$$

The possible mechanisms of TMP and TBP transformations in the $H_2/O_2/Ar$ flame are discussed.

INTRODUCTION

The combustion of organophosphorus substances (OPS) is of a great interest in connection with the disposal of toxic and hazardous chemical wastes and other undesirable substances that frequently contain these classes of compounds. One of the most promising techniques for the disposal of wastes is their incineration which provides a high destruction degree of toxic and hazardous substances. However, for better reliability and control over these processes one should know the details of the mechanism of their combustion and especially their chemistry. One of the typical representatives of the class of toxic OPS is the class of alkylophosphates. On the one hand, some of these are industrial wastes (e.g. tri-n-butylphosphate is the product of uranium ore treatment). On the other hand, these can be the models for studying the problems of the incineration of pesticides and the components of a chemical weapon. The chemistry of OPS combustion is practically not understood. The interest in the behavior of phosphorous containing substances in flames is not limited by the problem of their destruction. These substances (e.g. trimethylphosphate, phosphine) can play the role of inhibitors or promoters of the combustion process. These questions were the object of studies in references 1, 2, and 3. The aim of the present paper is to study 1) the behavior of trimethhylphosphate (TMP) and n-tributylphosphate (BP) as the simplest representatives of OPS in a well-studied flame of $H_2/O_2/Ar$ stabilized at low pressure on a flat burner and 2) the chemistry of reactions leading to the destruction of TMP in a flame by identifying intermediate and end products (including atoms and radicals) by their mass-spectra, measuring the concentrations and concentration profiles of initial, intermediate and end products. This could be the basis for developing the model of TMP combustion as one of the simplest OPS.

EXPERIMENTAL

The premixed $H_2/O_2/Ar$ (25,4/12,7/61,9) flames of a stoichiometric composition without additives and with TMP (0.034%) or TBP (0.04%) were stabilized at 80 Torr on a flat Spolding-Botha burner[4] 24 mm in diameter a brass disc with about 250 holes with diameter 0.7 mm each. The total consumption of the gas mixture was 65 cm/s (NTP). With such a burner, the flames at 80 Torr are sufficiently one-dimensional. A quartz cone, 15 mm high ,with an apex angle of 40 degrees, and a 0,17 mm diameter orifice, the width of walls at the top 0,15 mm was used. The probe was coupled with the flange of stainless steel cooled with water. TMP was

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supplied by a peristaltic pump or chromatographic syringe to the evaporator into the flow of preliminary mixed and heated to 85°C combustible mixture. Further the mixture passed to the burner. The temperature of the evaporator and the burner was kept equal to 85°C (in the case of TMP) or 150°C (in the case of TBP) with the help of a thermostat. Flame temperature was measured using a platinum - platinum with 10% rhodium microthermocouple weld of wires with a diameter of 50 microns and covered with a layer 10 microns thick. The thermocouple shoulder was 10 mm. The correction for radiation losses was introduced into the readings of the thermocouple. A molecular beam sampling technique coupled to a quadrupole mass-spectrometer was used for analysis of species and measurement of their concentrations in the flame.

The mass-spectrometric setup with molecular-beam sampling is partially described in reference 5. Synchronous detecting was used to record the modulated component of the molecular beam under ion-counting conditions. The modulation frequency was 12,5 Hz. The mass-spectrometer was supplied by an ion source with a small spread of electrons in energies ($\pm$ 0.1eV) which allowed us to work at low ionization energies close to the ionization potentials of atoms, radicals and molecules. The number of accumulations was 80-400. The concentrations of stable species are determined by direct calibration at ambient temperature by a procedure reported by Peeters and Mahnen[6]. The uncertainty in the stable species concentration is estimated as $\pm$ 10%.

RESULTS

The probe is known to perturb the flame. In this case the lines of equal concentrations near the probe tip shift relative to the unperturbed flame. The value of this shift can be estimated from the formula[7] $Z=0.4 D_o A_o(1/2)$, where D_o is the diameter of probe orifice; A_o is the sampling degree depending on the volumetric rate of sampling and the rate of the flow. For the flame described and the probe used, $Z=0,65$ mm. Although this value is small compared to the width of the combustion zone (2-3 mm), in the represented data this shift was taken into account. In the profiles of measured concentrations the origin of coordinates along the abscissa was put at the distance of 0,65 mm from the burner surface. Figures 1-3 show the data of the study of the structure of the above mentioned flames.

The data in Figure 1 are the experimentally measured profiles of temperature and concentrations of H_2, O_2, H_2O, and TMP in the flames with and without TMP. Figure 1 shows also TBP concentration profile in $H_2/O_2/Ar$ flame, doped with TBP. It is seen that small additions of TMP promote combustion process causing an appreciable decrease in the combustion zone width. The zone of TMP reacting is about 1,5 mm and is a bit narrower than that of oxygen and hydrogen in the flame. The same effect of promotion in the $H_2/O_2/Ar$ flame was observed at the addition of TBP. The zone of TBP reacting is a bit narrower than that of TMP. The chemistry of TMP transformations in the flame was studied by measurements of the profiles of peak intensities of masses related to the possible intermediate and end products of TMP transformations at low ionization energies close to the ionization potentials of these products. Several such products have been found. Figure 2 gives the profiles of mass peak intensities with m/e=32 (CH_3OH^+), 31 (CH_3O^+) 30 (CH_2O^+) and 140 (TMP^+) and 110 ($C_2H_7O_3P^+$) in the flame. These were measured for different U. The peak with m/e=110 is present in the TMP mass-spectrum as a fragmentary ion $C_2H_7O_3P^+$ with the appearance potential 11,9 $\pm$ 0.2eV[8]. With U=11.6 eV there is practically no contribution to the 110 peak of the fragmentary ion upon TMP ionization. So the m/e=110 peak intensity characterizes the concentration profile of the intermediate products resulting from TMP reacting. Such product can be represented either by DMP (dimethylphosphate ($CH_3O)_2P(O)H$) or DMP* (dimethylphosphite ($CH_3O)_2POH$) or their mixture. The possible reactions that can lead to the formation of DMP are the following:

$$(CH_3O)_3PO + H \Rightarrow (CH_3O)_2P(O)H + CH_3O$$
$$(CH_3O)_3PO \Rightarrow (CH_3O)_2P(O)H + CH_2O$$
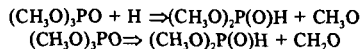
Preferable is the first one. The reaction of DMP isomerization leading to the formation of dimethylphosphite can proceed in parallel. This can, probably, account for the existence of the two maxima on the curve of ($C_2H_7O_3^+$). CH_3OH^+ and O_2^+ contribute to the peak with m/e=32. The contribution of O_2^+ was taken into account by measuring the peak with m/e=34 (oxygen isotope).

In the profile of peak intensity with m/e=32 in Figure 2 the contribution of O_2^+ ion is subtracted. This profile thus characterizes the concentration profile of CH_3OH. The CH_3OH formation can be explained by the reaction:

$$CH_3O + H_2 \rightarrow CH_3OH + H$$
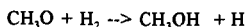
Because the intensity of this peak with m/e=31 (CH_3O) was measured with ionization energy

U=11,6 eV which is less than the potential of the appearance of this peak (PA=12,6 eV) in the mass-spectrum of CH_3OH, the profile of CH_3O^+ intensity in Figure 2 characterizes the concentration profile of CH_3O radical. The profile of the m/e=30 peak intensity characterizes the concentration profile of CH_2O, because the intensity of this peak was measured for an ionization energy U=16,5 eV, almost equal to the potential of CH_2O^+ ion appearance in the spectrum of CH_3OH (AP=16,3 eV). Note also the spatial separation of the concentration profiles of CH_3OH and CH_2O is pointing to the sequence of transformations upon CH_3OH oxidation in the flame.

Figure 3 presents the profiles of mass peak intensities with m/e=80 ($CH_5O_2P^+$, HPO_3^+), 64 (HPO_2^+), 63(PO_2^+), 48 (HPO^+) and 47 (PO^+) with U=13,1eV in the flame. Analyzing the behavior of these peaks in the flame, it is assumed that the contributions to the peak with m/e=47 of the PO^+ fragmentary ion, forming from PO_2, HPO_2, and HPO ionization, are rather small. Therefore the profiles of the intensities of mass peaks with m/e=47 and 64 characterize the concentration profiles of PO and HPO_2. The maximum in the profile of peak intensity with m/e=80 is in the range between two maxima in the peak intensity profile with m/e=110 which can be attributed to the formation of CH_5O_2P product due to DMP reaction or the reaction of DMP* with hydrogen atom. The behavior of the profiles of mass peak intensities with m/e=64, 63, 48, and 47 points to the following sequence of $H_xP_yO_z$ compound transformations in the flame:

$$HPO_2, PO_2 \Rightarrow PO$$

The errors in the measurements of the intensities of mass peaks in Figures 2 and 3 are: m/e=140 ±3%; m/e=110, 30, 32 ±10-20%; m/e= 47, 48, 63, 64 ±20%; and m/e= 31, 80 ±50%. The promoting effect of TMP on H_2/O_2 combustion can be explained as in reference 3 by the influence of phosphorous oxides on the reaction of H and OH recombination:

$$H + PO_2 \Rightarrow HOPO$$
$$OH + H_2 \Rightarrow H_2O + H$$
$$H + HOPO \Rightarrow H_2 + PO_2 .$$
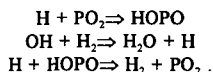
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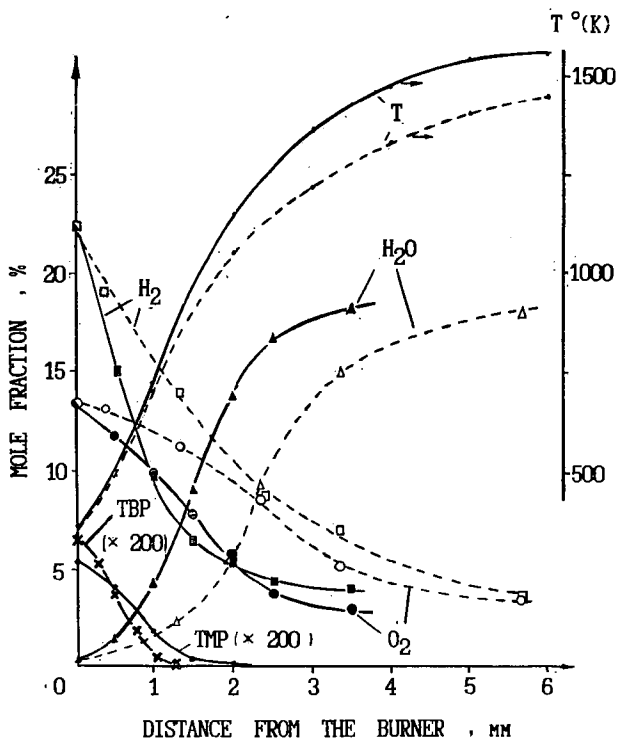8. Bafus, D.A.; Gallegos,E.J.; Kiser, R.W. *J. Phys. Chem.*, **1966**, *70*, 8, 2614-2619.

Fig. 1 The profiles of temperature and concentrations of components in H2/O2/Ar flame without additions:T,H2, O2, H2O - dotted lines; and with additions of TMP:T,H2, O2, H2O, TMP and with addition of TBP; TBP - solid lines.
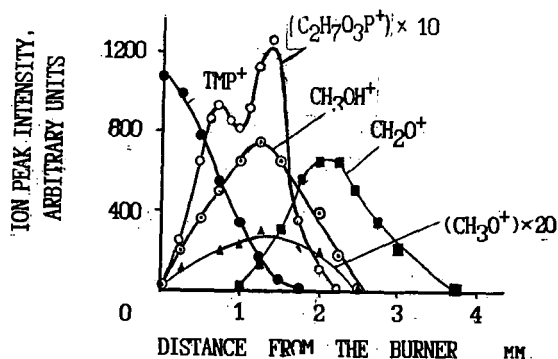
Fig. 2 The profiles of the intensities of mass peaks in the H2/O2/Ar flame with TMP additive with: m/e=32 (CH3OH+), U=13.1eV; m/e=140 (TMP+), U=13.1eV; m/e=31(CH3O+), U=11.6eV; m/e=30 (CH2O), U=16.5eV ; m/e=110(C2H7O3P+),U=11.6 eV
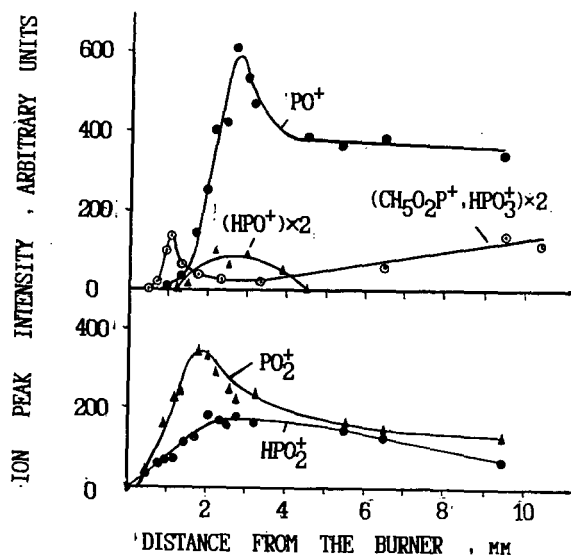

Fig. 3 The profiles of the intensities of mass peaks in the H2/O2/Ar flame with TMP additive with: m/e=47(PO+),48(HPO+), 63(PO2+), 64(HPO2+), 80(HPO3+, CH5O2P+). U=13.1eV.